## REMARKS

In this Amendment, Applicant has amended Claims 1 – 12. Claim 1 has been amended to specify different embodiments of the present invention and overcome the rejection. Claims 2 – 11 have been amended to proper dependent form and Markush group form. It is respectfully submitted that no new matter has been introduced by the amended claims. All claims are now present for examination and favorable reconsideration is respectfully requested in view of the preceding amendments and the following comments.

SPECIFICATION:

The abstract has been objected as containing informalities.

It is respectfully submitted that the informalities have been overcome. The abstract has been amended to a single paragraph. In addition, the term "mixing" has been corrected to "compatible with", because the term "mixing" is an incorrect English translation of the original term in Russian language of the original specification, which means the capability of being compatible with water (see page 5, line 17 – 19). Furthermore, in Example 1, a clerical error has been corrected by amending "94 wt.%" to "90 wt.%." It is respectfully submits that this error is clearly clerical as it is obvious to a person of ordinary skill in the art that the combination of granulated PA 6.66 and polyvinyl pyrrolidone should be 100%. Finally, the examples of Examples 2, 4, 6 and 10 have been correctly identified as comparison examples. It is respectfully submitted that no new matters have been introduced by the amendment.

Therefore, the objection to the abstract has been overcome. Withdrawal of the objection is respectfully requested.

CLAIM OBJECTIONS:



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Claims 4 and 7 have been objected as containing informalities.

It is respectfully submitted that the objection has been overcome by the current amendment. In particularly, Claims 4 and 7 have been amended to proper Markush group format according to the Examiner's suggestions.

Therefore the objection has been overcome and withdraw of the objection is requested.

REJECTIONS UNDER 35 U.S.C. § 112 SECOND PARAPGRAPH:

Claims 1 – 12 have been rejected under 35 U.S.C. § 112, second paragraph, as allegedly being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

It is respectfully submitted that the currently presented amendments clearly point out and define the embodiment of the present invention. More specifically, Claim 1 has been amended to specify that the 4.5-50.0 wt.% is based on the total weight of the film. The amendment is sufficiently supported by the examples in the specification.

In addition, Claim 6 has been amended to clearly define that the hydrophilic compound is low-molecular weight compound. Applicant respectfully submits that the term "low-molecular weight compound" in Claim 6 is definite to a person of ordinary in the art. In the Russian language, the term "low-molecular" is an established chemical and technical notion, well known and understandable to a person of ordinary in the art. In the English language, this notion corresponds the term "low molecular weight". The subdivision of substances into "low-molecular weight" and "high-molecular weight" ones is one of methods for classifying chemical compounds, used in chemistry, and also in polymer physics. Generally, substances having a molecular weight of less than $10^4$ Dal are conventionally regarded as low-molecular weight substances; while, substances having a molecular weight of the order of $10^4$—$10^6$ Dal and more are conventionally regarded as high-molecular weight substances. This subdivision is based on the fact that

the properties of low-molecular weight compounds are determined only by the chemical structure of the molecule. On the other hand, the properties of high-molecular weight compounds are determined by not only the chemical formula, but also, to a greater extent, by the average molecular weight, molecular weight distribution, and also by the pretreatment history.

Therefore, the rejection under 35 U.S.C. § 112, second paragraph, has been overcome. Accordingly, withdrawal of the rejections under 35 U.S.C. § 112, second paragraph, is respectfully requested.

REJECTIONS UNDER 35 U.S.C. § 102:

Claims 1 – 6 and 9 – 12 have been rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by both Strutzel et al. (US Pat. No. 4,243,074), hereinafter Strutzel. Claims 1 – 2, 4 – 8 and 12 have been rejected under 35 U.S.C. §102(b) as allegedly being Julius (US Pat. No. 3,329,509), hereinafter Julius.

Applicant traverses the rejection and respectfully submits that the presently claimed invention is not anticipated by the cited reference. More specifically, Claim 1 has been amended to define "a single-layer polymer film for food products, comprising a polyamide matrix and a component providing high permeability of the film with respect to smoke substances and water vapors, wherein said component is a hydrophilic compound in an amount of 4.5-50.0 wt. % of the total weight of the film, and said hydrophilic compound: i)_forms in the polyamide matrix a highly dispersed phase with a linear domain size of 0.1-3.0 μm in a direction perpendicular to a surface of the film in the polymide matrix, and ii) is compatible with at least 10 wt. % of water." These features are not disclosed or suggested by Strutzel or Julius. Claims 2 – 12 also include these features due to their dependence on Claim 1.

STRUTZEL:

Although Strutzel describes a tubular packaging material, preferably for use as a sausage casing, it mainly discloses a multi-layer tubular packaging material having two or more layers, comprising a tubular packaging arrangement comprised of a packaging material comprising at least one first layer of a polymer comprising a linear polyamide and, bonded to the outer surface of said first layer, at least one second layer of a polymer comprising a major proportion of a linear polyamide containing from about 2 to 40 percent by weight of a hydrophilic substance compatible with the polyamide, said hydrophilic substance comprising polyvinyl alcohol (Claim 1 of Strutzel). Strutzel **does not state that the hydrophilic compound is a component providing** high **permeability to both smoke substances and water vapors.**

In addition, the subject matter of Strutzel is a tubular packaging material based on a polyamide, **having at least two layers**. The subject of the present invention is a single-layer polymer film comprising a polyamide matrix and a component providing high permeability **to smoke substances and water vapors**

The problem to be solved by Strutzel is to provide a tubular packaging material which has improved **barrier properties** (i.e., essentially **impermeability**), first of all, with respect to oxygen and **water vapors** and does not form wrinkles after scalding (column 3, paragraph 1, lines 3—8). The object of the present invention is to provide a film which has **high permeability** with respect to smoke substances (phenol permeability) **and** water vapors (vapor permeability), i.e., the problem to be solved is exactly the opposite one (see paragraph [009]). As regards the barrier properties with respect to oxygen, the problem posed in the present application is <u>to preserve them</u> "at least at the level of the polyamide matrix", but not to improve them.

The problems to be solved by Strutzel arise from the purpose of the casings: the casings according to Strutzel are intended for **cooked** sausages. The casings according to the present invention are intended for **smoked** and **air-dried** sausages, thereby a **radical difference** being required in the permeability properties of the casings with respect to smoke substances (phenol permeability) and/or water vapors (vapor permeability).

Besides, the properties of the multilayer film are essentially influenced by the composition and properties of each of the film layers. Each layer of the film imparts thereto properties inherent to said layer, i.e., impermeability with respect to one or another substance (see, for example, equations 1—6 from the paper by S.E. Solovyov, A.Ya. Goldman "Permeability of multi-layer structures", e-Polymers No. 023. The text can be downloaded from the page http://www.e-polymers.org/abstract.cfm?abstract_id=664#, copy enclosed). This regularity is widely employed in designing barrier packaging films, when for imparting to the film impermeability for a particular substance, a layer is incorporated into the film composition, made of a material with corresponding properties (see, e.g., US 6541087 — Abstract, Claims, US 5185189 — Abstract, Claims, etc.). Therefore, the permeability of the film according to Strutzel is limited by the permeability of the first polyamide layer which does not comprise polyvinyl alcohol (claim 1 of the set of claims).

Furthermore, the Examiner indicated that the film being capable of mixing with at least 10 wt.% of water, according to Strutzel. In the amended claims, the limitation "compatabile with at least 10 wt.% of water" relates **only** to the hydrophilic compound.

Finally, the reference contains no mention about **highly dispersed phase of the hydrophilic compound with domains of certain size within the polyamide matrix of the film layer comprising polyvinyl alcohol**.

In summary, Strutzel and the present application describe polymer films having different purpose, different structure, composition as a whole, and properties.

JULIUS:

Julius deals with films (casings) which must have a required degree of permeability for water vapors (column 1, lines 51—53). In this document, however, numerical values of the permeability for water vapors, which would allow the properties of the films to be compared, are not indicated. In the present application, besides the required degree of permeability for water vapors, the firm must have a high permeability

with respect to smoke substances as well. However, this property is not disclosed in Julius. Therefore, the problems to be solved in Julius and in the present application are different.

Regarding the Examiner's conclusion that to the film produced in accordance with Julius, high permeability with respect to smoke substances and a highly dispersed phase with a linear domain size of 0.1—3.0 μm are inherent, this conclusion cannot be agreed. The assertion that "products having a similar composition cannot have mutually exclusive properties" is not correct for high-molecular weight compounds (polymers) and compositions of materials. High-molecular weight compounds are characterized by the chemical composition and structure of one unit of the macromolecule, by the structure of the macromolecule as a whole (linear, branched), by the periodicity of the units, by the molecular weight, by the molecular-mass distribution, by the geometry and stereometry of the macromolecule. Compositions are characterized by the qualitative composition (ingredients) and quantitative composition (concentration of the ingredients), by the structure of the composition and by the structure of the ingredients; the structure of the composition and of the ingredients is determined by the method for preparing the composition. The films according to the claimed invention are made from a composition of high-molecular compounds. Therefore, even in case films are made from compositions having a similar formulation, the properties and structure of these films will be different, since the methods for preparing the compositions and the corresponding films are different.

The terms "polyamide", "polyvinyl alcohol" and "cellulose ethers" denote large families of polymers having different monomeric composition and a wide spectrum of properties. In particular, polyvinyl alcohols (PVAs) may contain in their macromolecules various amounts of residual vinyl acetate units (assessed by the degree of saponification or hydrolysis). Polymers with a high degree of saponification (more than 97%) are almost insoluble in cold water, but they are soluble in hot water. Polymers with a low degree of saponification (70—90%) are readily soluble in cold water (see, for example, the brochure KSE of the present owner of the PA mark "Mowiol": http://www.kuraray-am.com/pvoh-pvb/downloads/Mowiol_brochure_en_KSE.pdf, page C1, sections C 2.2

and C 2.3; drawings 1—9 and 13—18, copies of related pages enclosed). Into the membrane or casing according to Julius, "hydrophilic but water-insoluble ingredients" are incorporated, and PVAs suitable as such ingredients are defined as "insoluble in cold water, though soluble in hot water" (page 1, column 2, lines 19—22). Consequently, they are PVAs with a high degree of saponification. In present application, it is shown (see Example No. 4) that such marks of PVAs do not meet the condition of forming a highly dispersed phase in polyamide 6.66 (on the contrary, a coarsely dispersed phase is formed), and film from their mixture with the polyamide is not sufficiently permeable for smoke substances and water vapors to provide smoking effect.

Therefore, the Examiner's conclusion that in the film according to Julius "polyvinyl alcohol forms a highly dispersed phase in polyamide" is not supported by the established facts. On the contrary, an example of embodying the present invention is a mixture from polyamide and a PVA with a reduced degree of hydrolysis (see Example No. 3), soluble in cold water.

Among hydrophilic cellulose ethers, there are both water-insoluble and water-soluble ones. However, the present application claims only such nylon/cellulose ether mixtures which meet the condition of a highly dispersed phase of the hydrophilic component being formed irrespective of their solubility. Thus, the present invention is not disclosed or suggested by Julius.

Therefore, the newly presented claims are not anticipated by Strutzel or Julius and the rejection under 35 U.S.C. § 102(b) has been overcome. Accordingly, withdrawal of the rejection under 35 U.S.C. § 102(b) is respectfully requested.

<u>REJECTIONS UNDER 35 U.S.C. § 103</u>:

Claims 7 – 8 have been rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over Strutzel in view of Julius.

Applicant traverses the rejection and respectfully submits that the embodiments of present-claimed invention are not obvious over Strutzel in view of Julius. The significant differences between the present invention and Strutzel or Julius have been discussed as above.

It is respectfully submitted that not all hydrophilic compounds have an ability to enhance the polyamide film permeability with respect to water vapor and phenol. The specification and the set of claims of the present invention highlight two distinctive features which hydrophilic compounds suitable for attaining the claimed technical result must have. The first distinctive feature is the ability of the hydrophilic compound to absorb at least 10% of water of its mass. The second distinctive feature is the ability to form in the polyamide matrix a highly dispersed phase with a linear domain size of 0.1—3.0 μm. The first distinctive feature that "a hydrophilic compound capable of being compatibile with at least 10% of water" can be understood by referring to the explanation in the specification -- "Compatibility is understood to mean the capability of two or more components to form liquid or solid systems that are homogeneous on a molecular level. This concept includes both the swellability and solubility" (page 5, lines 17 – 19). The necessity for the hydrophilic additive to satisfy **both** distinctive conditions **simultaneously** is seen also from the exemplary preferable embodiments of the invention presented in the present application, such as, Examples 8 and 10, and also the corresponding permeability values listed in the Table.

With regard to aluminum silicates, they cannot be used as the hydrophilic additive for attaining the technical result claimed in the present application, because, as is known to a person of ordinary skill in the art, aluminum silicates absorb water in amounts substantially less than 10% (the household embodiment of aluminum silicate is porcelain) and belong neither to the category of hydrophilic polymers, nor to the category of water-soluble salts which constitute the concept "hydrophilic substance" according to the interpretation given in the present application (claims 4—6). On the other hand, soluble salts, according to Julius, are not claimed as a self-contained additive for improving the permeability for water vapors of the film-forming agent and are used only in combination with 'the hydrophilic but water-insoluble ingredient".

Besides, a person having ordinary skill in the art cannot know a priori, whether aluminum silicate will form in the polyamide matrix a highly dispersed phase with a linear domain size of 0.1—3.0 μm or not.

Due to above indicated differences, there is no motivation or reasonable expectation of success to combine Strutzel with Julius. Therefore, Even if they are combined, a person of ordinary skill in the art will not discern the present invention at time of its invention.

In summary, the newly presented claims are not obvious over Strutzel in view of Julius. The rejection under 35 U.S.C. § 103 has been overcome. Accordingly, withdrawal of the rejections under 35 U.S.C. § 103 is respectfully requested.

Having overcome all outstanding grounds of rejection, the application is now in condition for allowance, and prompt action toward that end is respectfully solicited.

Respectfully submitted,

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Enclosures:

1. S.E. Solovyov, A.Ya. Goldman "Permeability of multi-layer structures", e-Polymers No. 023;
2. The brochure KSE of the "Mowiol" Polyvinyl Alcohol.

e-Polymers **2004**, no. 023.

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# Permeability of multi-layer structures

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*Abstract:* In this paper we show that 'permeability' of a heterogeneous structure with mass transport and thermodynamic properties varying across its thickness is a misleading concept leading to incorrect results and design decisions while two structural transmission rate equations are recommended for practical applications. The notion of structural identity of multi-layer films is introduced to explain the apparent failure of the 'permeability' concept. Structural identity of two or more films means the same material sequence in the structure relative to separated environments with constant relative thickness of each corresponding layer. Structurally identical films indeed have the same 'permeability', however the notion of identity is shown to contradict the practical goals of multi-layer film design. Engineering examples are provided to demonstrate potential misuses of the 'permeability' concept in practical multi-layer design decisions. Correct problem statements and calculation procedures are included. Some general limitations of transmission rate equations are also discussed. These include the role of boundary conditions, temperature and concentration dependence of permeant diffusivity and solubility in a polymer matrix, the presence of co-permeants, surface sorption effects, film thickness, homogeneity of polymer matrix for permeation purposes and correct utilization of available data for predicting gas transport properties of multi-layer films.

## 1. Introduction

Prediction of water vapour and gas transmission rates through layered plastic structures is critical in design and manufacturing of barrier packaging. Unlike gas separation membranes used to efficiently separate gas mixture components, barrier packaging designs are intended to reduce mass transport rates of undesirable gases and vapours across the barrier and ultimately to extend the packaged product shelf life. Multi-layer packaging materials are predominantly produced as films and sheets via processes like co-extrusion and lamination to utilize unique performance properties of several materials in a single product. A recent paper by Cooksey et al. [1] summarized equations suggested in various package-engineering references for calculating permeability and transmission rates of atmospheric gases through multi-layer films in steady state. It also recommended specific equations depending on

desired applications and available experimental data. These equations formalized model calculations of transmission rate and 'permeability' of heterogeneous structures comprised of sequential homogeneous layers with uniform thicknesses and applied to specific permeating species.

Four types of equations were introduced: calculation of transmission rate of the heterogeneous structure from either transmission rates or permeabilities of individual layers, and calculation of 'permeability' of the structure from the same two data subsets. While the steady state transmission rate of a permeant across a heterogeneous structure when a fixed permeant pressure difference is imposed on opposite sides of the barrier is a valuable and universally accepted concept, the concept of 'permeability' of a heterogeneous structure is shown to not withstand close scrutiny. Also, when trying to apply the structural permeability equations to particular package design problems, the concept of 'permeability' of multi-layer structures causes confusion in interpretation of results within the packaging community. Clearly several clarifications are in order.

## 2. Definitions

Transmission rate (*TR*) also called *permeance* refers to the amount of permeant $q$ passed through the unit area $A$ of tested film sample in unit time $t$ under unit pressure difference $\Delta p$ of permeating species across the film thickness and specified conditions of temperature $T$ and relative humidity RH at the film surfaces (according to ASTM procedures D1434-82 for gases, D3985-02 for oxygen, E96-00e1 and F372-99 for water vapour in ref. [2]). Film thickness $L$ is not a part of *TR* definition but is implied to be the film sample thickness. Permeability $P$ of material to specific permeant is its transmission rate normalized to a unit film thickness, usually 1 mil (= 0.001 inch = 25.4 μm) in the US. Thus, *TR* and $P$ are formally defined as

$$TR = \frac{q}{At\Delta p} \tag{1}$$

$$P = \frac{qL}{At\Delta p} = TR \cdot L \tag{2}$$

Units commonly used in package engineering in the United States for $P$ and *TR* of gases are

Permeability $P$: $\mathrm{cc(STP) \cdot mil / (100\ in^2 \cdot 24\ h \cdot atm)}$ at temperature $T$ and RH

Transmission rate *TR*: $\mathrm{cc(STP) / (100\ in^2 \cdot 24\ h \cdot atm)}$ at temperature $T$ and RH

while corresponding SI units for gases are

Permeability $P$ (common): $\mathrm{cm^3(STP) \cdot mm \cdot m^{-2} \cdot day^{-1} \cdot bar^{-1}}$ at $T$ and RH

(reference): $\mathrm{m^3(STP) \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}}$

Transmission rate *TR* (common): $\mathrm{cm^3(STP) \cdot m^{-2} \cdot day^{-1} \cdot bar^{-1}}$ at $T$ and R

(reference): $\mathrm{m^3(STP) \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}}$

Here the pressure difference in atm (1 atm ≡ 101.325 kPa), bar (1 bar ≡ 100 kPa), or Pa refers to the external pressures of the gaseous permeating species on the opposite sides of the membrane.

Permeability $P$ and transmission rate *WVTR* of water vapour are usually measured in grams of permeated water [3]:

Permeability $P$: g · mil / (100 in$^2$ · 24 h) at temperature $T$ and RH difference in air (or other carrier medium) at 1 atm of air pressure on both sides of the membrane

Transmission Rate $WVTR$: g / (100 in$^2$ · 24 h) at temperature $T$ and RH difference in air at 1 atm

The relative humidity difference across the membrane thickness is usually specified between some relative humidity value of atmospheric air (e.g., 60, 65, 75, 80, 85, 90, 100% RH were reported in ref. [3]) and 0% RH on the opposite side of the membrane. For concentration dependent diffusion when the diffusivity and $TR$ of the permeant across a membrane depend on the local concentrations of the permeant dissolved in the membrane, both boundary conditions (absolute gas pressures or RH outside the membrane) must be specified. The same should be done in case of multi-component diffusion when the presence of co-permeants affects the diffusion and $TR$ of the permeant in question. The RH of permeating gas is included in the standardized $TR$ measurement conditions for this very reason since many polar polymers are plasticized by water resulting in significant structural and corresponding permeant $TR$ changes. The most common example is ethylene-vinyl alcohol copolymer (EVOH) that exhibits very strong dependence of oxygen transmission rate ($OTR$) across it on RH of oxygen gas. To report $OTR$ of EVOH when RH gradient is present across the membrane, RH at both surfaces of the membrane must be specified rather than just the RH difference since the data will differ dramatically for, say, RH pairs 0 - 40% and 60 - 100% corresponding to the same RH difference of 40% across the membrane.

We note that the amount of permeant $q$ is expressed in moles (mol) or as its mass in grams (g) used mostly for water vapour permeation, but for permanent gases in package engineering it is commonly referred to in cc (cm$^3$) at STP, i.e., at 0°C and 1 atm of pressure.

## 3. Equations

Equations suggested for total transmission rate $TR_T$ and total permeability $P_T$ of a multi-layer structure with $N$ layers denoted A, B, ..., N assuming homogeneity and uniform thickness of each layer are categorized in ref. [1] from package engineering refs. [4-7] and reproduced below. All these equations are derived from Fick's laws of diffusion assuming constant and equal permeant fluxes through all layers at steady state conditions and low concentrations of permeating species to invoke Henry's law on linear dependence of permeant partial pressure on its concentration. When concentration dependence of diffusion, nonlinearity of sorption isotherms and the effects of co-permeants on transport properties of materials can be neglected, the details of the derivation are trivial and can be found in most package engineering textbooks. We will only discuss the final equations.

### *3.1 Calculating transmission rate from transmission rate data*

$$TR_T = \frac{1}{\frac{1}{TR_A} + \frac{1}{TR_B} + \ldots + \frac{1}{TR_N}} \tag{3}$$

This equation does not involve material permeabilities and layer thicknesses and does not lead to confusion in practice. Transmission rate of any particular layer is used regardless of uniformity of layer chemical composition and molecular structure.

For example, layers A and B can be considered a single layer identified as AB and $TR_{AB}$ is measured. Then we can write

$$TR_T = \frac{1}{\frac{1}{TR_{AB}} + \frac{1}{TR_C} + \ldots + \frac{1}{TR_N}} \tag{4}$$

If layers A and B are physically separate and uniform in their respective thickness and molecular structure, it is also true that

$$TR_{AB} = \frac{1}{\frac{1}{TR_A} + \frac{1}{TR_B}} \tag{5}$$

If materials A and B are blended however, then their molecular structure changes and Eq. (5) does not apply, but Eq. (4) is still valid, provided $TR_{AB}$ of the AB blend is measured.

### *3.2 Calculating transmission rate from permeability data*

$$TR_T = \frac{1}{\frac{L_A}{P_A} + \frac{L_B}{P_B} + \ldots + \frac{L_N}{P_N}} \tag{6}$$

Eq. (6) is essentially equivalent to Eq. (3) when each layer is made from a material of uniform chemical composition and molecular structure with known $P$.

### *3.3 Calculating permeability from permeability data*

$$P_T = \frac{L_T}{\frac{L_A}{P_A} + \frac{L_B}{P_B} + \ldots + \frac{L_N}{P_N}} \tag{7}$$

Here the total structure thickness: $L_T = L_A + L_B + \ldots + L_N$.

### *3.4 Calculating permeability from transmission rate data*

$$P_T = \frac{L_T}{\frac{1}{TR_A} + \frac{1}{TR_B} + \ldots + \frac{1}{TR_N}} \tag{8}$$

Eqs. (7) and (8) relating individual material ($P$) and layer ($TR$) data to permeability $P_T$ of multi-layer structure are the ones causing confusion in interpretation of results. The reason for that is an underlying assumption that it is possible to normalize the transmission rate of the whole structure to a unit thickness and thus obtain the structure 'permeability' according to permeability definition. Let us discuss the validity of this $TR$ normalization assumption.

## 4. Structural identity

In an ideal world, where we are able to vary any layer thickness within a structure at will and maintain the relative thickness of all layers constant, the $TR$ normalization

assumption is undoubtedly true. Constant relative thickness of layer $Z$ meaning $L_Z/L_i$ $= const$ for any $L_i$ as we vary $L_Z$, i.e., thickness of all other layers $L_i$ along with the total thickness $L_T$ must change in proportion to $L_Z$ change. We call the constant relative layer thickness property of multi-layer films a *structural identity*. Two or more films are structurally identical (broad definition) when exposed to identical pairs of distinct environments they separate, if they possess the same number and material sequence of layers relative to the separated environments as well as equal relative thickness of each corresponding layer. Strictly, for any layer number $Z$ in both films 1 and 2 numbered from the same external environment both films exposed to, it must be made from the same material X having the same morphological structure and the relationship $L_{Z1}/L_{T1} = L_{Z2}/L_{T2}$ must be maintained for these films to be considered structurally identical in the given broad sense. Consider the following example of four multi-layer structures with corresponding layer thicknesses (arbitrary units) exposed to the identical pairs of distinct environments (say, fixed 'left' and 'right' environments):

| | | | |
|---|---|---|---|
| Structure 1. | Material sequence: | A-B-C-A | |
| | Layer thickness: | 4 1 2 3 | Total: 10 |
| Structure 2. | Material sequence: | A-B-C-A | |
| | Layer thickness: | 8 2 4 6 | Total: 20 |
| Structure 3. | Material sequence: | A-B-C-A | |
| | Layer thickness: | 4 2 2 3 | Total: 11 |
| Structure 4. | Material sequence: | A-B-A-C | |
| | Layer thickness: | 4 1 3 2 | Total: 10 |

According to the given definition, films 1 and 2 are structurally identical even though their total thicknesses differ. On the other hand, pairs 1-3 and 2-3 are structurally different since the relative thickness of layer B in film 3 (and all other layers as well) is not the same as in film 1 or 2, namely $L_B/L_T = 1/10$ for films 1 and 2 while $L_B/L_T = 2/11$ for film 3. Film 4 is different from all others because it has a different material sequence. In fact, even mirror symmetrical films like

| | | | |
|---|---|---|---|
| Structure 5. | Material sequence: | (Env. 1) A-B-C-D (Env. 2) | |
| | Layer thickness: | 1 2 3 4 | Total: 10 |
| Structure 6. | Material sequence: | (Env. 1) D-C-B-A (Env. 2) | |
| | Layer thickness: | 4 3 2 1 | Total: 10 |

i.e., the same film with asymmetric layer structure exposed to the same distinct environments 1 and 2 will not in general exhibit the same mass transport behaviour when the material sequence of layers is reversed. The already mentioned effects including concentration dependent diffusion, multi-component diffusion with coupled co-permeant effects, and nonlinear sorption isotherms discussed later are responsible for this asymmetry. Hence, in general the structures 5 and 6 are not structurally identical in the broad sense when the environments they separate are taken into account, although in a narrow sense one can call them structurally identical from, say, manufacturing viewpoint when the surrounding environments are not considered. Obviously, the membrane with symmetric (material and thickness) layer structure like

| | | | |
|---|---|---|---|
| Structure 7. | Material sequence: | A-B-C-B-A | |
| | Layer thickness: | 1 2 3 2 1 | Total: 9 |

will exhibit no dependence on the environmental differences on its opposite sides, and it can be reversed resulting in the same transmission rates of the permeant in question.

It is clear from the examples above that if we vary only one or several (but not all) layer thicknesses to satisfy some new design goals then we change the structural identity of the new film compared to the original (rather than its thickness only). The attempt to use the total permeability $P_T$ in Eqs. (7) or (8) even for simple engineering tasks involving structural changes will then lead to incorrect results. Later in the article examples 2 and 3 demonstrate inapplicability of the *TR* normalization assumption to structurally different films.

In real world each layer has a specific practical purpose such as gas barrier, water vapour barrier, adhesive, food contact layer, etc., and that fact does not warrant a change in its thickness as we vary thickness of one particular layer. In other words the change in one layer thickness to meet a practical goal usually does not involve changing the thickness of other layers. Thus, in engineering practice we are not interested in maintaining the structural identity of the film as we improve its structural design. Therefore the stated *TR* normalization assumption is invalid in practice since it applies only to structurally identical films. There are also technological and practical limitations to arbitrarily changing layer thickness, e.g., the adhesive layer thickness (usually about 0.3 - 1.0 mil in packaging films) cannot be significantly reduced due to co-extrusion process limitations and loss of interlayer adhesion nor can it be increased due to deterioration of mechanical properties and economic reasons.

## 5. General discussion

To illustrate the point made above let us consider an example calculation in ref. [1] taken from the *Handbook of Package Engineering* by Hanlon et al. [4].

*Example 1*

Tab. 1. Three-layer laminate of the following structure is considered:

| Layer | Materials | $L$ / mil | *OTR* | *P* |
|---|---|---|---|---|
| 1 | Material 1 | 1.5 | 500 | 750 |
| 2 | PVDC | 0.5 | 0.05 | 0.025 |
| 3 | Material 2 | 2.0 | 1200 | 2400 |

Here *OTR* is the oxygen transmission rate in cc / (100 in$^2$ · 24 h · atm) at 77°F (25°C) and 50% RH and pressure gradient of 1 atm of pure oxygen across the membrane, and *P* is the material oxygen permeability in cc · mil / (100 in$^2$ · 24 h · atm) at the same conditions added by us for reference using Eq. (2). The permeated oxygen amount is expressed in cc (cm$^3$) at STP.

What are $TR_T$ and $P_T$ of this laminate? We would want to know both its actual field performance and permeability value on 1 mil basis for comparison with published data for other structures. Using Eq. (3) we correctly determine the total oxygen transmission rate through this laminate (4 mil thick) as

$TR_T = 0.05$ cc / (100 in$^2 \cdot$ 24 h $\cdot$ atm) (9)

If we try to calculate the permeability of this laminate using Eq. (8), we obtain

$P_T = 0.20$ cc $\cdot$ mil / (100 in$^2 \cdot$ 24 h $\cdot$ atm) (10)

which is exactly the same result as reported in ref. [1]. What is the value of this result? Presumably we can compare our laminate with another material or multi-layer structure on 1 mil to 1 mil basis and conclude that one outperforms another, however this comparison is meaningless. The reason is simple: single polymer material can be processed into film of almost any thickness, but our laminate is a prefabricated article with thickness of 4 mil. The same laminate 1 mil thick with proportional reduction of each layer thickness to maintain its structural identity and hence its predicted $P_T$ = 0.20 cc $\cdot$ mil / 100 in$^2 \cdot$ 24 h $\cdot$ atm simply is not available and quite possibly cannot be made at a reasonable cost if at all (it has to have the following structure: 0.375 mil Material 1 + 0.125 mil PVDC + 0.5 mil Material 2). Thus, any speculation about its normalized properties is in vain until such a hypothetical structure materializes.

A careful practitioner will avoid such a pitfall simply by using Eqs. (3) and (6) for *TR* calculation and comparison of multi-layer structures instead of trying to compare meaningless normalized properties like $P_T$ according to Eqs. (7) or (8). But it is one thing to report such data for comparison purposes (no matter how confusing) and quite another to base package design decisions on such calculations. The real danger lies in the attempt to use Eqs. (7) and (8) for solving practical engineering problems as demonstrated in the following examples.

*Example 2*

Consider the same structure as in Tab. 1, but now our task is to reduce laminate *OTR* by 50% by increasing PVDC layer thickness. What will be the new PVDC layer thickness to achieve that goal? In this simple scenario it is intuitively obvious that since PVDC provides nearly 100% of laminate barrier properties, we need to increase its thickness two fold to achieve the desired total transmission rate reduction. This fact is easily demonstrated using Eq. (3):

$$TR'_T = \frac{1}{\dfrac{1}{TR_1} + \dfrac{1}{TR'_2} + \dfrac{1}{TR_3}} \qquad (11)$$

where $TR'_2$ and corresponding PVDC layer thickness $L'_2$ are unknown, while the new target transmission rate is obtained from result (9):

$TR'_T = 0.5\ TR_T = 0.025$ cc / (100 in$^2 \cdot$ 24 h $\cdot$ atm) (12)

Using Eq. (12) and solving Eq. (11) for $TR'_2$ we obtain

$$TR'_2 = \frac{1}{\dfrac{1}{0.5 \cdot TR_T} - \left(\dfrac{1}{TR_1} + \dfrac{1}{TR_3}\right)} \qquad (13)$$

or $TR'_2 \approx 0.5\ TR_T = TR'_T = 0.025$ cc / (100 in$^2 \cdot$ 24 h $\cdot$ atm).

Then, to obtain $L_2$ we use Eq. (2):

$L'_2 = P_2 / TR'_2$ (14)

resulting in $L'_2$ = 1.0 mil. The new laminate structure is 4.5 mil thick:

| Layer | Material | $L$ / mil |
|---|---|---|
| 1 | Material 1 | 1.5 |
| 2 | PVDC | 1.0 |
| 3 | Material 2 | 2.0 |

which is exactly the result we expected. That confirms the validity of Eq. (3) for package design purposes.

Let us now try Eq. (7) to reproduce this result. We denote the increase in layer 2 thickness as $\Delta L$, then the unknown new PVDC layer thickness is

$$L'_2 = L_2 + \Delta L \tag{15}$$

Now we attempt to reduce the total permeability $P_T$ of the laminate by 50% in a manner similar to Example 1 (presumably to improve the total transmission rate of the laminate by 50% as an unstated goal) taking into account the increase in both $L_2$ and $L_T$ by $\Delta L$:

$$P'_T = 0.5 \cdot P_T = \frac{L_T + \Delta L}{\dfrac{L_1}{P_1} + \dfrac{L_2 + \Delta L}{P_2} + \dfrac{L_3}{P_3}} \tag{16}$$

Solving Eq. (16) for $\Delta L$ we obtain

$$\Delta L = \frac{L_T}{P_T \cdot \left( \dfrac{1}{P_2} - \dfrac{1}{0.5 \cdot P_T} \right)} \tag{17}$$

or $L = L_T/6 = 0.667$ mil and, correspondingly, new $L'_2 = 1.167$ mil. This result is quite different from the earlier obtained 1.0 mil, however when we substitute formula (17) or its numerical solution into Eq. (16) we see that it is the correct solution of the problem as stated. When we calculate the total transmission rate of this new laminate using Eq. (3), the result is

$$TR'_T = 0.0214 \text{ cc} / (100 \text{ in}^2 \cdot 24 \text{ h} \cdot \text{atm}) \tag{18}$$

which is a 57% reduction in laminate total *OTR* and is 14% below the target *OTR*. Let us try another structure from practical applications to check whether this discrepancy is always small and can be neglected in engineering applications.

*Example 3*

Tab. 2. The following laminate is considered:

| Layer | Materials | $L$ / mil | *OTR* | *P* |
|---|---|---|---|---|
| 1 | Material 1 | 1.5 | 80 | 120 |
| 2 | Material 2 | 1.5 | 0.016 | 0.024 |
| 3 | Material 3 | 1.0 | 1000 | 1000 |

at some temperature and relative humidity. The engineering goal is the same: to reduce structural *OTR* by 50% by changing the thickness of (primary oxygen barrier) layer 2. From Eq. (3), the total transmission rate of this 4 mil thick structure is

$$TR_T = 0.016 \text{ cc} / (100 \text{ in}^2 \cdot 24 \text{ h} \cdot \text{atm}) \tag{19}$$

while its permeability is found using Eq. (8):

$$P_T = 0.064 \text{ cc} \cdot \text{mil} / (100 \text{ in}^2 \cdot 24 \text{ h} \cdot \text{atm}) \tag{20}$$

Using result (13), the new transmission rate of layer 2 is

$$TR'_2 \approx 0.5\, TR_T = TR'_T = 0.008 \text{ cc} / (100 \text{ in}^2 \cdot 24 \text{ h} \cdot \text{atm}) \tag{21}$$

and the corresponding new layer 2 thickness is

$$L'_2 = P_2 / TR'_2 = 3.0 \text{ mil} \tag{22}$$

This is the expected correct result that suggests to double the thickness of the primary barrier layer. Now we try to use Eq. (7) to reproduce it. Using Eqs. (15) and (16) we attempt to reduce the total permeability $P_T$ of the structure by 50% to obtain

$$P'_T = 0.5\, P_T = 0.032 \text{ cc} \cdot \text{mil} / (100 \text{ in}^2 \cdot 24 \text{ h} \cdot \text{atm}) \tag{23}$$

leading to result (17) for the layer 2 thickness increase $\Delta L$ = 6 mil, and, correspondingly,

$$L'_2 = L_2 + \Delta L = 7.5 \text{ mil} \tag{24}$$

When we calculate $TR'_T$ of the new structure using Eq. (3), the result is

$$TR'_T = 0.0032 \text{ cc} / (100 \text{ in}^2 \cdot 24 \text{ h} \cdot \text{atm}) \tag{25}$$

which is an 80% reduction in the total structure *OTR* and 60% below target *OTR* – enormous overkill compared to the stated goal also implying prohibitive material waste.

Let us understand what went wrong when we used Eq. (7). In attempt to reduce the permeability $P_T$ of the total structure, i.e., normalized $TR_T$, we designed a laminate that on 1 mil thickness basis is 50% better than the old one with the implicit assumption of proportional reduction of each layer thickness to maintain its structural identity. In example 2, when the actual redesigned 4.667 mil thick laminate was analyzed we saw that its real world performance ($TR_T$) was improved by 57% due to thicker than necessary PVDC layer. Thus, we had to waste unnecessary material because of the incorrectly stated goal of improving $P_T$ of reference 1 mil structure suggested by Eq. (7) instead of $TR_T$. The discrepancy in example 3 was even more pronounced. The point made earlier, however, is that no such ideal 1 mil thick 'reference' structure exists nor it is practical to make for any purpose. The actual laminate will never be 1 mil thick since it is impossible to reduce all layer thicknesses without compromising the useful properties of this film such as mechanical properties, regulatory limitations on food contact layer thickness, etc. That supports our earlier assertion that it is meaningless to compare multi-layer structures on basis of their 'permeability' or transmission rates normalized to unit thickness.

The correct way to state the original design problem and utilize the concept of 'permeability' of heterogeneous layered structure should have been: how to reduce the overall *OTR* of the laminate by 50% by *proportionally changing the thickness of all layers*, rather than the primary barrier layer. Now we deal with structurally identical films and the answer is trivial: double the total film thickness by doubling the thickness of all layers. However, practical experience leads us to the conclusion that

the layer thickness selection is independent from each other since each layer in a package structure serves a different purpose. The situation in which all layer thicknesses are proportionally changed to maintain the structural identity of the film does not correspond to real world development efforts since the goal of structural design improvement can be formulated as *changing the structural identity of the existing design* to achieve a new level of performance. Thus, maybe it is time to stop reporting 'permeability' values for multi-layer and other heterogeneous structures that are not structurally identical as this approach is clearly misleading.

The same problem arises when we attempt to use Eq. (8) for solving examples 2 and 3 since it is not $P_T$ that must be routinely improved but $TR_T$. Therefore, any equation where $P_T$ of multi-layer structure is used for calculation of film component properties will produce incorrect results unless the structural identity of the modified structure is strictly maintained, and that is simply not practical and leads to confusion. In fact, new ASTM Standards D1434-82 (updated in 1998) and D3985-02, respectively, for gas and oxygen permeability testing of plastic film and sheeting specifically refer to *permeability* only when homogeneous materials are considered [2]. For heterogeneous structures only gas transmission rates can be determined. It is also worth noting that the authoritative references and textbooks on packaging engineering and technology [4-7] and even monographs on diffusion mathematics [8] routinely use Eqs. (7) and (8) in discussing permeability of layered heterogeneous structures further clouding the presented concepts.

Another implication of using Eqs. (7) and (8) for engineering purposes is that the resulting Eq. (16) may lead to physically meaningless results (division by zero) at some combinations of parameters. That situation is never present when Eqs. (3) or (6) are used for *TR reduction* purpose. Of course, if one attempts to *increase* $TR_T$ by varying one layer thickness, meaningless results are possible with Eqs. (3) and (6) since other layers may provide sufficient barrier to permeation to prevent $TR_T$ increase to a target value even with zero thickness of the selected layer. In the following section we will discuss general limitations of the steady state transmission rate approach and will refer only to Eqs. (3) and (6) as relevant for package design purposes.

## 6. Other limitations

Eqs. (3) and (6) are derived from Fick's first law of diffusion relating flux of the matter $J_x$ to its concentration gradient (more precisely, the gradient of chemical potential of the diffusing species) in $x$ direction:

$$J_x = -D\frac{dc}{dx} \tag{26}$$

which can be considered a steady state or instantaneous case of Fick's second law of diffusion relating concentration change in time to spatial concentration gradients (one dimensional version with concentration independent diffusivity $D$ is shown):

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{27}$$

Here $c = c(x,t) = [A]_M$ is the concentration of the permeating species A in the material M, and $D \equiv D_{AM}$ is the diffusivity of permeant A in material M assumed to be independent of concentration $c$. The permeability $P$ of a gas in a solid is defined as a product of the gas diffusivity $D$ and its solubility coefficient $S$ in the solid matrix:

$$P = D \cdot S \tag{28}$$

That follows from the solution-diffusion mechanism of permeation originally proposed by Graham [9]. The book by Vieth [10] provides a more comprehensive review of gas and vapour diffusion mechanisms in different types of polymers although it stops short of deriving equations analogous to (3) and (6) for multi-layer structures. Eqs. (26) and (27) deal with the permeant concentrations in the material; hence to convert the concentrations to partial gas pressures outside the membrane Henry's law may be used:

$$c = S \cdot p \tag{29}$$

The solubility coefficient $S = S_{p,T}$ of gaseous permeant A in material M is the equilibrium thermodynamic property relating the equilibrium permeant concentration in the material to its partial pressure in the adjacent gas phase:

$$S_{p,T} \equiv \left(S_M^A\right)_{p,T} = \frac{[A]_M}{p_{A,gas}} \tag{30}$$

The permeant is said to obey Henry's law if $S_{p,T}$ as defined in Eq. (30) is constant for the range of pressures of interest from 0 to $p^*$.

The correct way to treat solubility of gases in solid media in direct contact with each other as present in multi-layer polymer structures is to introduce the partition coefficient $H$ of the permeant between these media as a ratio of equilibrium concentrations of the permeant A in materials M and N:

$$H \equiv H_{MN}^A = \frac{[A]_M}{[A]_N} \tag{31}$$

which in general depends on absolute values of permeant pressures in the materials. Due to low solubility of gases in most polymers, the gas-polymer solutions can be considered dilute and Henry's law applies in most cases. Since partial pressures (more accurately, activities) of A have to be the same in both materials if they are in equilibrium, the concentrations in Eq. (31) can be replaced by respective solubilities of A in materials M and N using Henry's law (29):

$$H_{MN}^A = \frac{S_M}{S_N} \tag{32}$$

There are few notes to be made regarding the applicability of these equations in the general sense. Material and gas interaction properties $D$ and $S$ depend on temperature, and for most materials the regular Van't Hoft-Arrhenius dependence can be assumed [11]:

$$D = D_0\, exp\left(\frac{-E_D}{RT}\right) \tag{33}$$

$$S = S_0\, exp\left(\frac{-\Delta H_S}{RT}\right) \tag{34}$$

where $E_D$ is the activation energy of diffusion, and $\Delta H_S$ is the molar heat of sorption. If the concentration of permeant in a gas phase in direct contact with the solid is $c_0$, then the steady state concentration of the permeant $c_1$ in the solid right across the phase boundary is

$$c_1 = c_0 \exp\left(\frac{-\Delta H_S}{RT}\right) \quad (35)$$

This type of dependence is valid unless the solid material undergoes physical changes when the temperature $T$ is altered. Glass transition, change in crystallinity, melting, deformation, and relaxation of molecular orientation imposed by a processing technique are several examples of such changes in polymer systems. Even at the same temperature, different crystallinity and morphological structure of a polymer imparted by the processing method are some of the reasons why the measured permeability of an annealed injection molded plaque might be different from that of a rapidly cooled film of the same thickness extruded with a high draw ratio. While viscoelasticity of solid polymers manifesting itself in time-dependent responses to deformation and relaxation of molecular structure far from equilibrium is a widely studied area [12-14], its effects on transport properties of polymers especially related to oxygen and water vapour diffusion are largely unknown [10]. In case of very thin films, the sorption properties of the film surface and structural defects (like pinholes) may also introduce nonlinearity of the transmission rate dependence on the film thickness.

Apart from Van't Hoft-Arrhenius dependence of $D$ and $S$ on temperature, the diffusivity $D$ of a particular gas is known to be affected by the presence of co-permeants (if a mixture of different gases is present), while the solubility $S$ is often a nonlinear function of external pressure, and there is a solubility limit for many polymer-gas systems at high pressures [10,11]. The linear relationship suggested by Henry's law and the diffusivity independence of the sorbed permeant concentration in Fick's first law hold only when 'permanent' gases like nitrogen, oxygen, hydrogen and carbon dioxide are permeants, and the gas pressure is nearly atmospheric. When interactions of gas with polymer become important, other types of sorption are often observed like Langmuir, Flory-Huggins and BET sorption isotherms [11]. The sorption isotherm type greatly affects the permeation behaviour as a function of external pressure. Therefore caution should always be exercised when calculating total transmission rates using Eqs. (3) and (6) at conditions far from those at which transmission rates for individual structural layers were obtained, or different processing methods were used in manufacturing multi-layer structures and homogeneous material samples for transmission rate measurements.

A note is due on homogeneity of materials for transmission rate measurement. With rapid development and commercialization of heterogeneous materials like polymer composites filled with inorganic particulates, we need to distinguish between heterogeneous materials and heterogeneous structures. All preceding discussion dealt with layered structures, i.e., the heterogeneous structures consisting of clearly defined distinct layers made from different materials. The structure of the material forming a single layer was not considered, and its permeability and transmission rate for the specific permeating species were treated as given. While it is true that polymer composites may exhibit gas and vapour transmission rates much different from those of an unfilled polymer matrix, this approach to permeability of a *single layer* is still valid if the particulate is finely (and, in a sense, 'homogeneously') dispersed in the polymer matrix. More precisely, if

a) the characteristic size of the dispersed particles is much smaller than the layer thickness

b) the particles are dispersed randomly without discernible agglomeration in the matrix

c) the volume fractions of the dispersed particles are the same in bulk polymer and at the layer surfaces

d) particle orientation in bulk and at the layer surfaces is the same, e.g., random or oriented (orientation is essential only if the particles possess quantifiable uniformly irregular shapes, e.g., constant high aspect ratio circular or rectangular platelets)

then we may consider the composite material as 'homogeneous' for permeability purposes and use its gas transport properties in multi-layer film equations (with the corresponding sorption isotherm behaviour changes due to filler presence, if any). 'Homogeneous' for permeability purposes simply means that with all other properties being constant, any change in the layer thickness without violating conditions a - d will result in the inversely proportional change in the measured transmission rates according to Eq. (1) and satisfying Eq. (2). In case of high aspect ratio particles in clay filled nanocomposites, particle orientation relative to layer thickness direction will significantly affect measured transmission rates. Such a material even if still considered 'homogeneous' will not be isotropic for gas permeation. Hence, all gas transport properties exhibited by it will be diffusion direction specific: that should be taken into account when using single layer permeability data for analysis of gas transmission through a multi-layer structure containing such composite materials.

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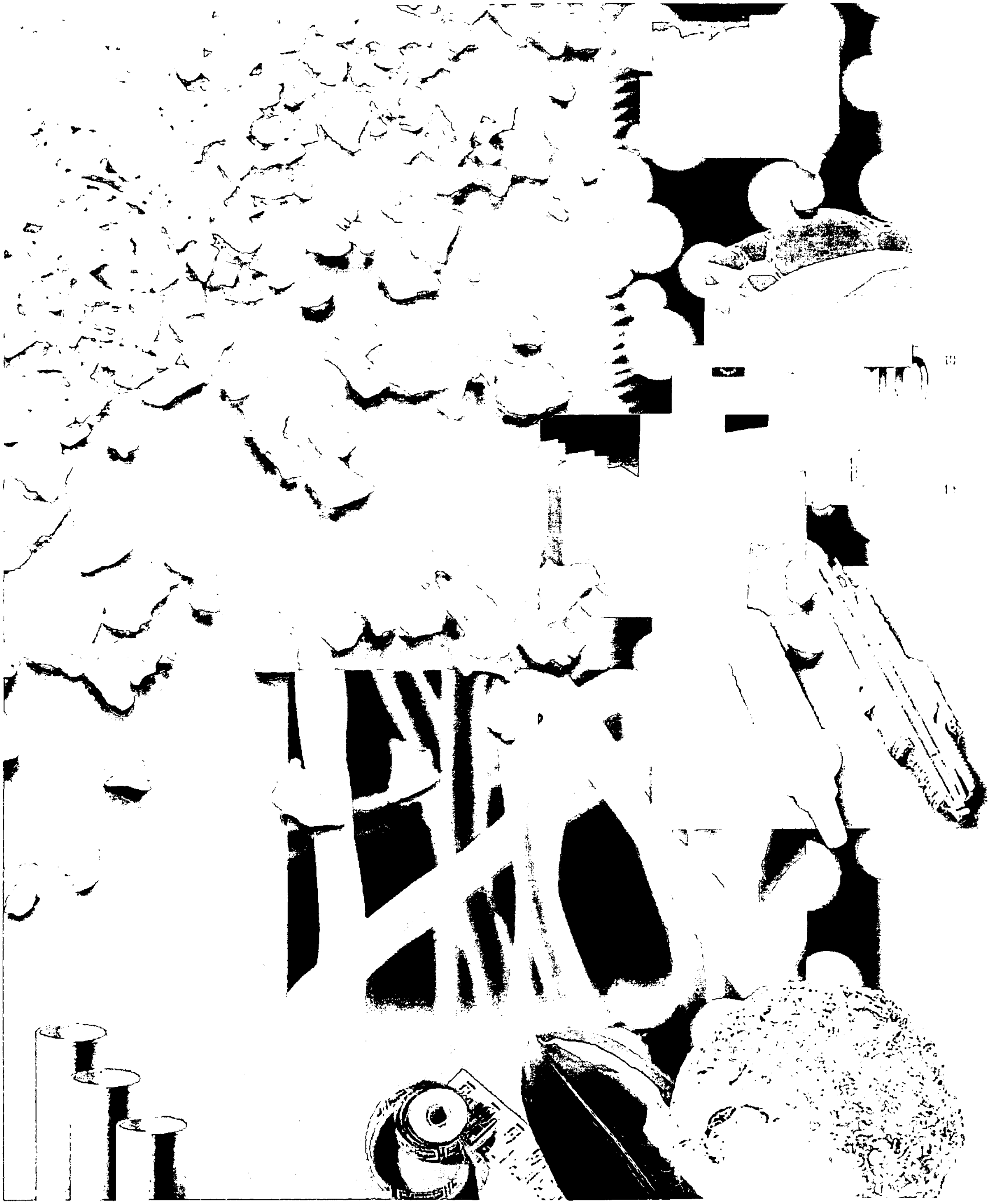

# ®Mowiol

## Polyvinyl Alcohol

Water is the most commonly used and technically most important solvent for polyvinyl alcohol.
The dissolving procedure is simple, especially for Mowiol granules.

The photograph shows starting product, dissolving procedure and solution.

| | | Page |
|---|---|---|
| 1 | Solubility of Mowiol | C 1 |
| 2 | Determination of the relative Rate of Dissolution of Mowiol | C 1 |
| 2.1 | Partially hydrolysed Mowiol Grades | C 1 + C 2 – C 6 |
| 2.2 | Fully hydrolysed Mowiol Grades | C 1 + C 7 – C 10 |
| 2.3 | Rate of Dissolution of Mowiol Grades | C 1 + C 2 – C 10 |
| 3 | Industrial Production of Mowiol Solutions | C 11 |
| 4 | Other Solvents and Diluents for Mowiol | C 11 |

Water is the most common solvent for polyvinyl alcohol and, for practical applications, the most important.

The solubility of Mowiol in water can be defined as the quantity of Mowiol which dissolves at a certain temperature in a given time in comparable apparatus (dissolving curve).
It is natural feature of polymers that the production of a »saturated solution« is impossible, as for each grade an increase in concentration is accompanied by a rise in solution viscosity, the limit to which is set by that solution's industrial processability (see Section D 2).

**Literature**

*A Harréus, W Zimmermann*, Hoechst AG/Resin News *19*, 24 (1983)

The relative rate of dissolution of Mowiol can be determined in the laboratory equipment described below:

180 g of deionized water at about 20 °C is poured into a 500 ml three-necked flask fitted with a reflux condenser and impeller stirrer. 20 g of the Mowiol to be tested are sprinkled through a powder funnel during stirring (manual operation of the agitator used). The weight of volatile constituents must be taken into account. When the filling process is completed, the flask is placed in a thermostatically controlled water bath and the contents are stirred at about 250 $min^{-1}$. The start of agitation is taken as the zero point of the dissolving-time measurement.

Experience shows that the water bath has to be heated to 95 – 99 °C *to give the required temperature of 90 °C in the dissolver.* The latter temperature is reached in a few minutes.

10 % solutions are produced to standardize the experiments.

Because the diffusion of the water molecules in solvation is relatively slow and heavily dependent on viscosity, higher concentrations naturally require longer dissolving times.

Every five minutes, one drop of the solution is removed by capillary pipette and used to determine the solution concentration by refractometry (see Section D 2.1). From these values the dissolving characteristics of a Mowiol grade can be plotted on the relevant concentration/time graph.

Towards the end of the dissolving process a visual check must be made to determine clarity, specks and freedom from lumps.

To determine further aspects of the various Mowiol grades' dissolving properties, this process can also be used at temperatures below 90 °C (eg at 60, 40 and 20 °C).

As a general rule, a fall in the degree of polymerization and hydrolysis is accompanied by a rise in the rate of dissolution in water, as is clearly evident at different dissolving temperatures.

In fully hydrolysed polyvinyl alcohols the effect of the degree of polymerization is generally more pronounced than in partially hydrolysed ones. Polymers whose level of hydrolysis is below 88 % are more soluble in water at low temperatures than at high temperatures.

*Figures 1 to 11* show the rate of dissolution and dissolving properties of partially hydrolysed Mowiol grades, measured by the method described in Section C 2.

In the case of low-viscosity Mowiol 4-88 the graph shows that at 20 °C after a sufficient time (30 min in the test) approx 96 % of the polymer has gone into solution. The still undissolved components are in the form of highly swollen, soft particles (lumps) which are very difficult to remove from the solution by filtration. At about 90 °C, however, they dissolve without trace. It is also possible to separate out the lumps by decanting or centrifuging.

Mowiol grades with a high residual acetyl content show different dissolving behaviour (cloud point).

*Figures 12 to 19* show how important it is to maintain the dissolving temperature of 90 °C, especially in dissolving the fully hydrolysed Mowiol grades. The dissolving curves show that in the temperature range 40 – 60 °C the granules do start to swell but scarcely dissolve at all. Only when this temperature is exceeded are they likely to dissolve properly. Completely clear and speck-free solutions are finally obtained at 90 °C.

*Figures 1 to 18* on the following pages refer to the production of solutions with a target concentration in water of 10%.

*In each case the values were measured on a single batch.*

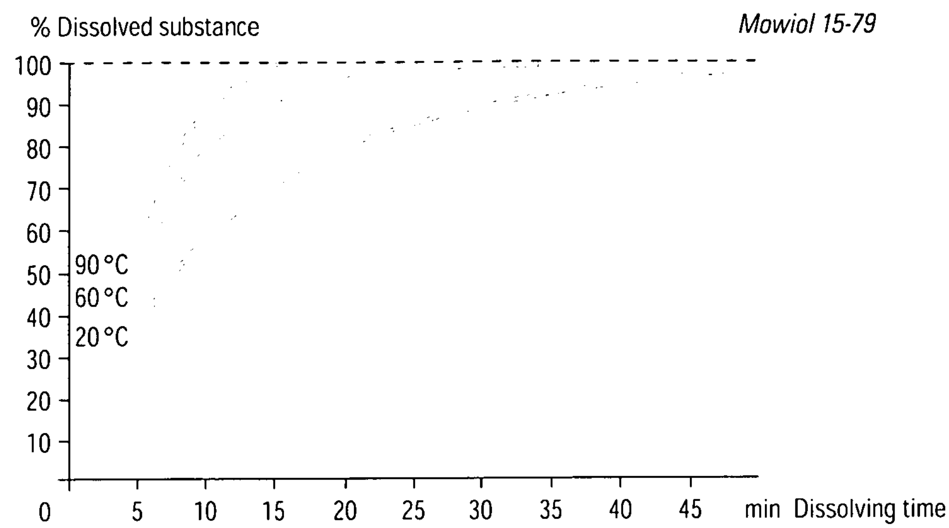


*Figure 1 Rate of dissolution of Mowiol 15 – 79*

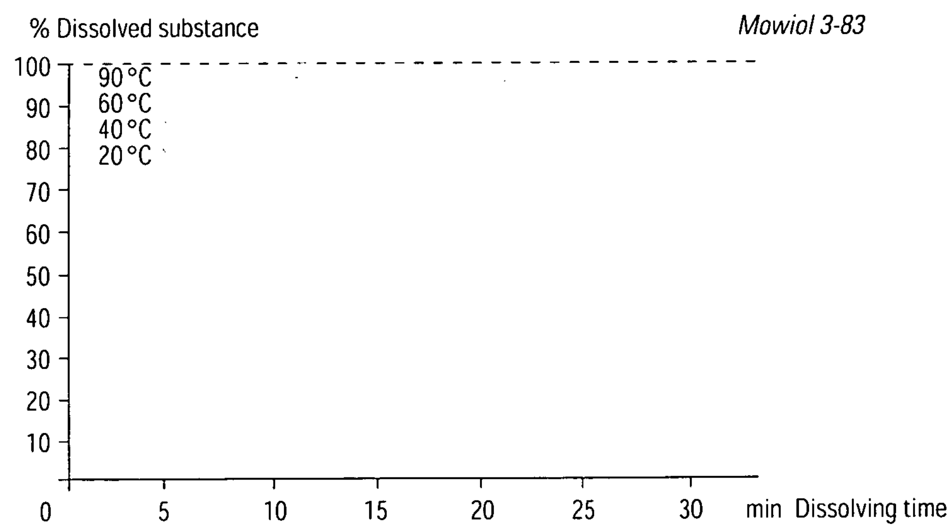


*Figure 2 Rate of dissolution of Mowiol 3 – 83*

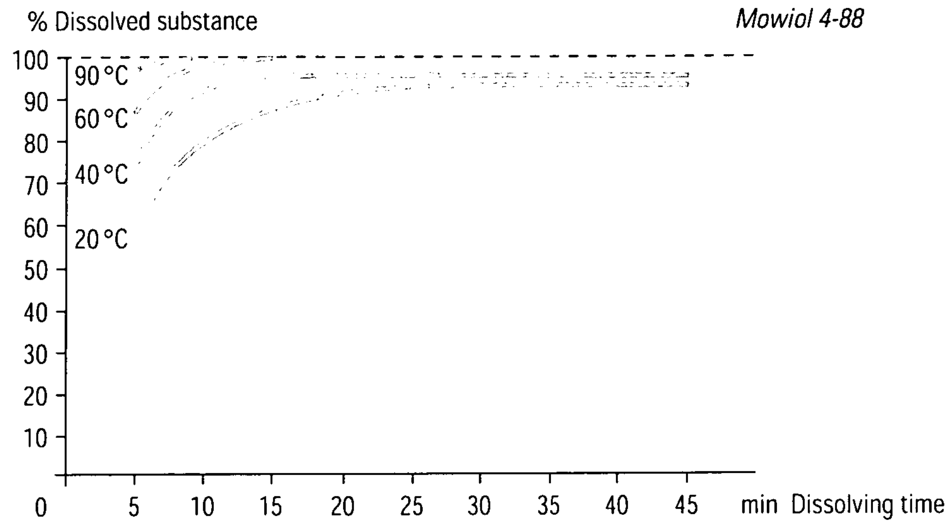


*Figure 3 Rate of dissolution of Mowiol 4 – 88*

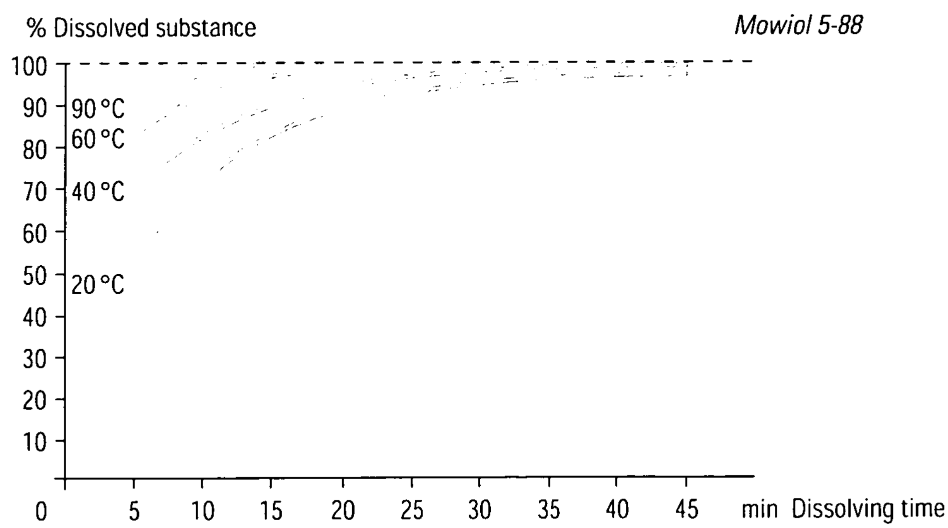


*Figure 4 Rate of dissolution of Mowiol 5 – 88*

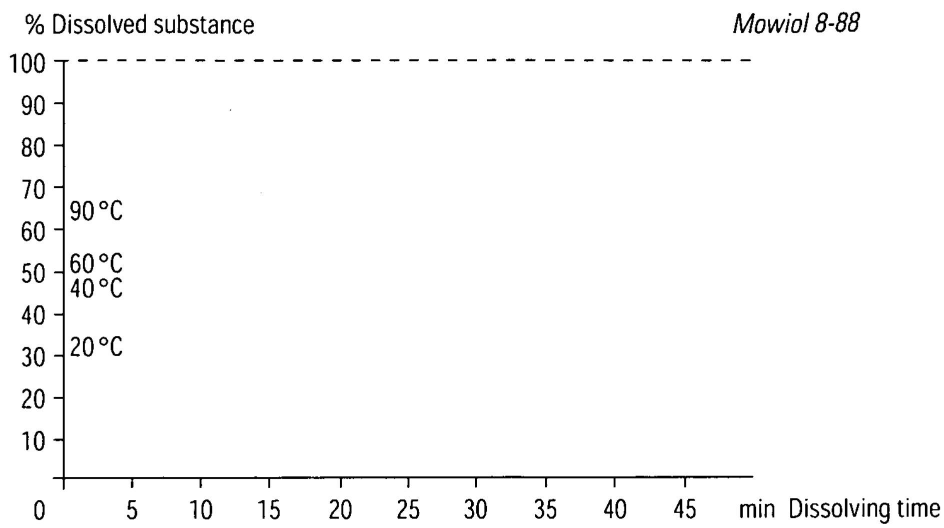


*Figure 5 Rate of dissolution of Mowiol 8 – 88*

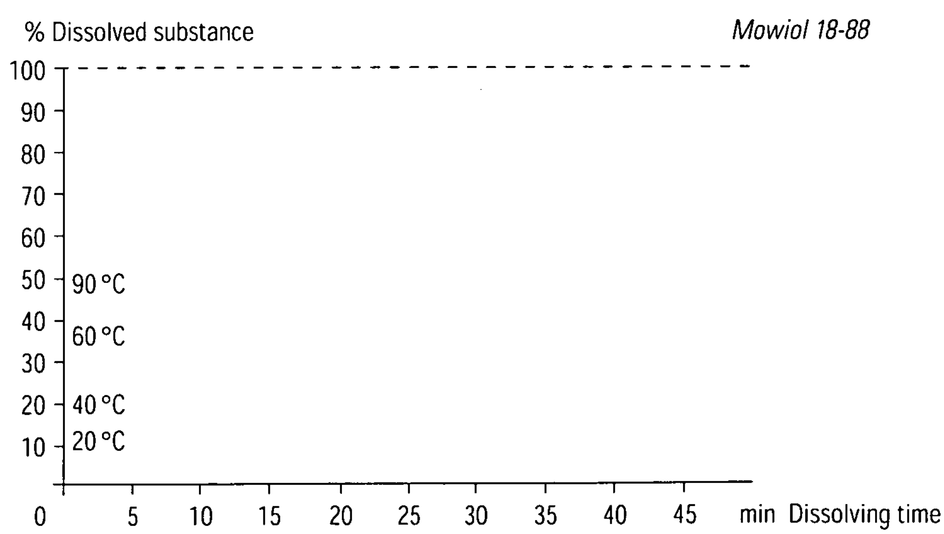


*Figure 6 Rate of dissolution of Mowiol 18 – 88*

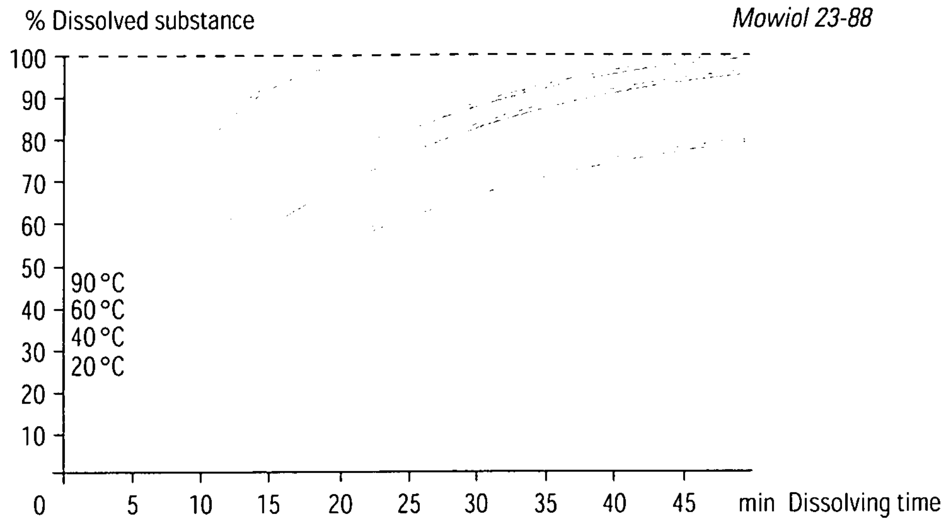


*Figure 7 Rate of dissolution of Mowiol 23 – 88*

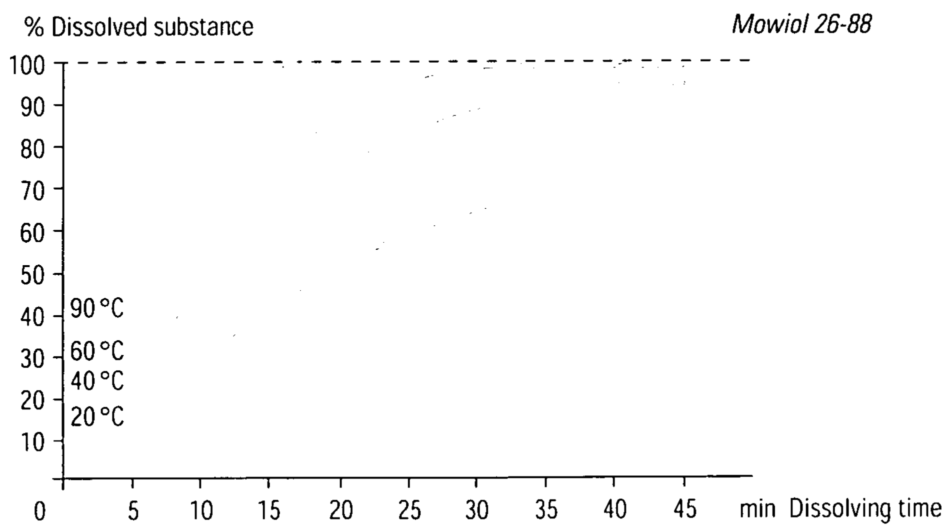


*Figure 8 Rate of dissolution of Mowiol 26 –88*

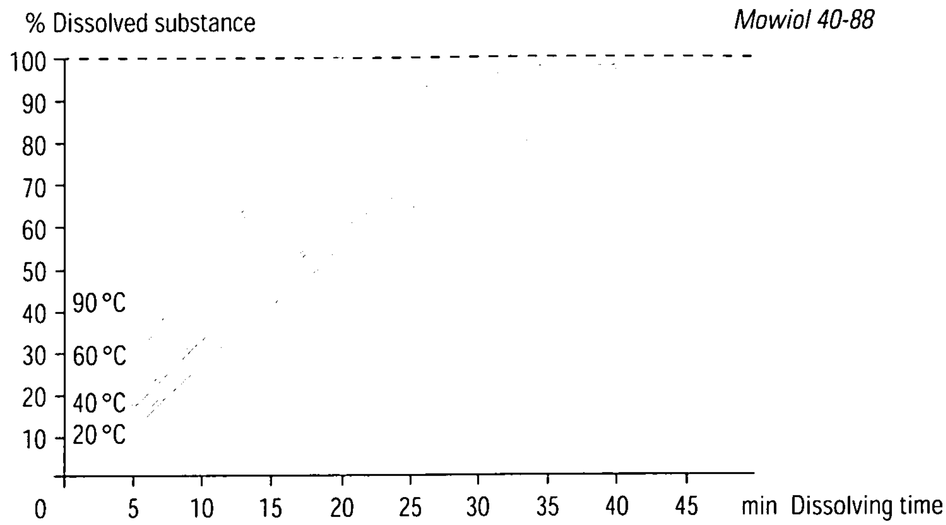


*Figure 9 Rate of dissolution of Mowiol 40 – 88*

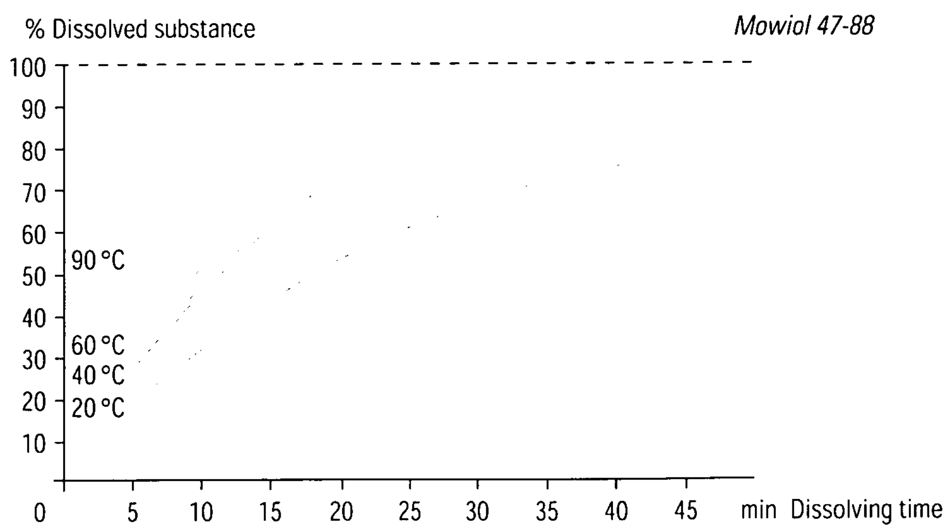


*Figure 10 Rate of dissolution of Mowiol 47 – 88*

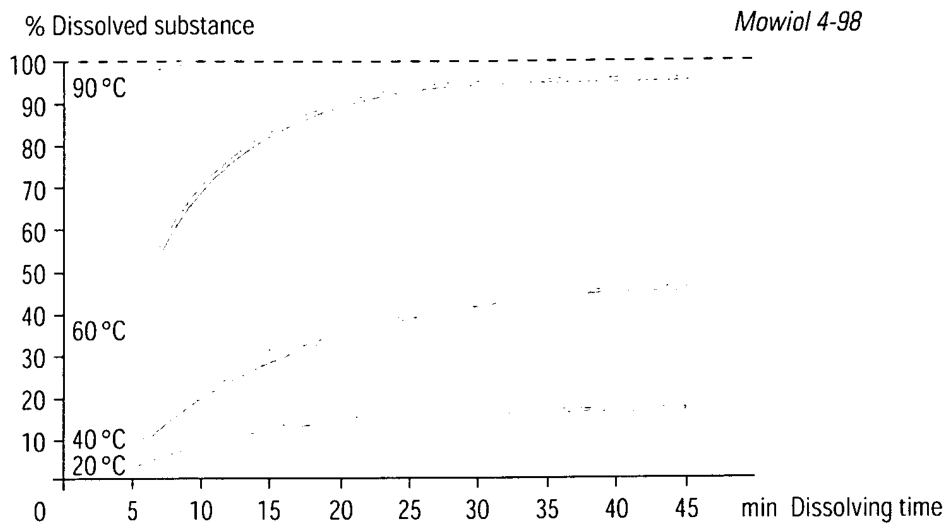


*Figure 13 Rate of dissolution of Mowiol 4 – 98*

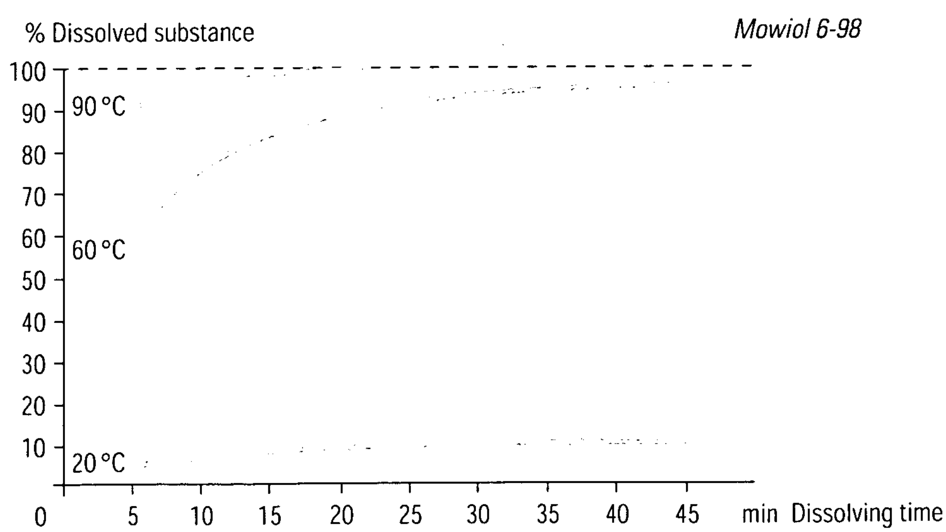


*Figure 14 Rate of dissolution of Mowiol 6 – 98*

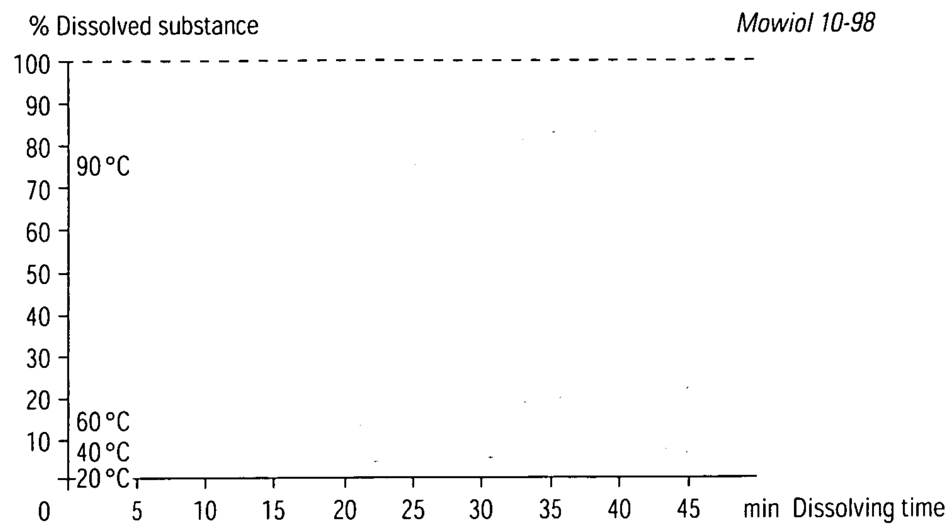


*Figure 15 Rate of dissolution of Mowiol 10 – 98*

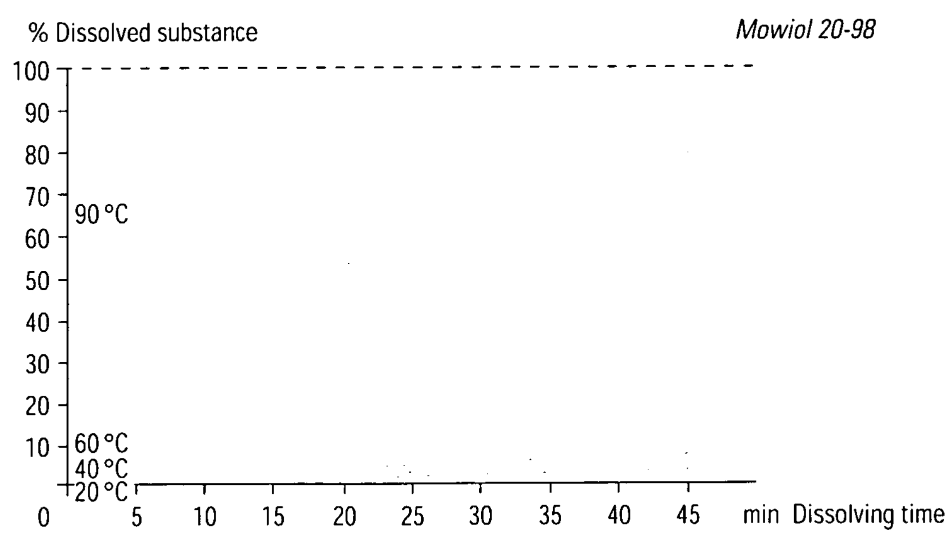


*Figure 16 Rate of dissolution of Mowiol 20 – 98*

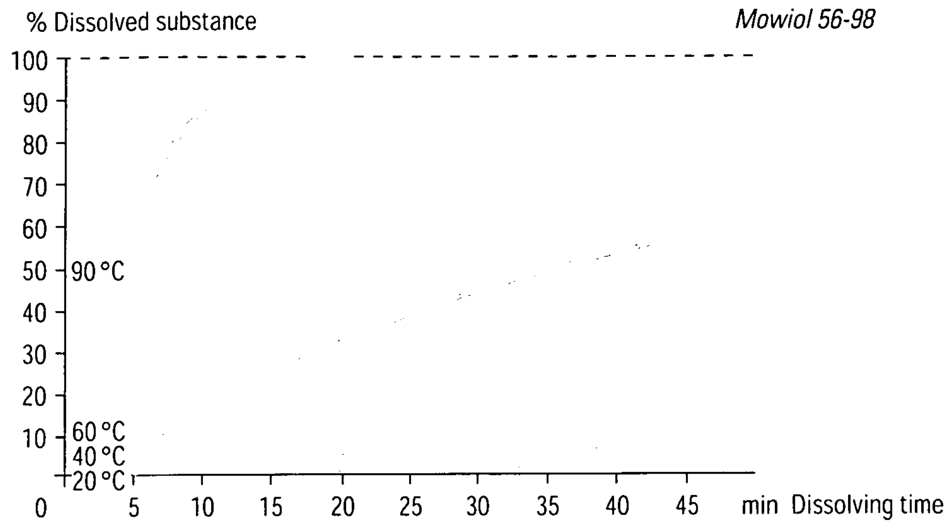


*Figure 17 Rate of dissolution of Mowiol 56 – 98*

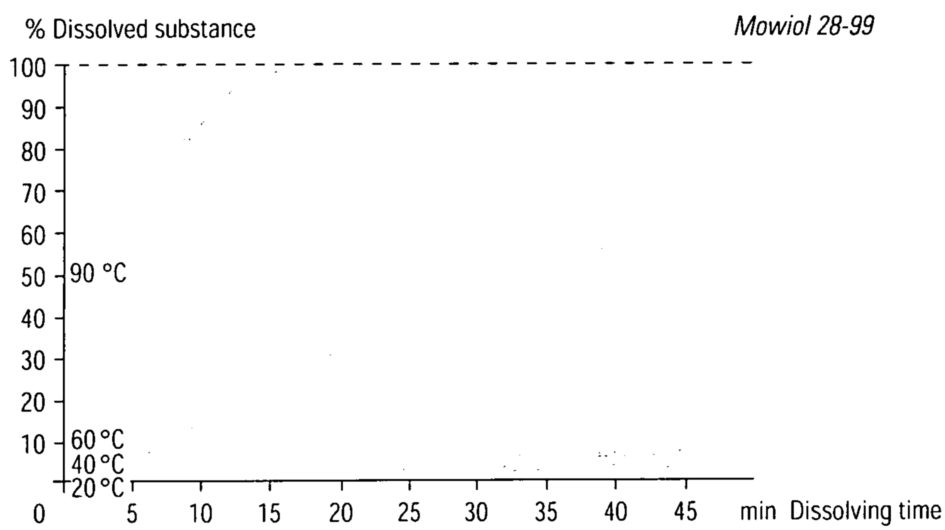


*Figure 18 Rate of dissolution of Mowiol 28 – 99*

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